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(54) Title: SYNTHETIC FUEL WITH REDUCED PARTICULATE MATTER EMISSIONS AND A METHOD OF OPERATING A COMPRESSION IGNITION ENGINE USING SAID FUEL IN CONJUNCTION WITH OXIDATION CATALYSTS

(57) Abstract: The invention provides a compression ignition engine fuel derived from a Fischer-Tropsch process, which fuel has a generally increasing iso:n paraffins ratio with increasing paraffin carbon number at least between C9 to C18, less than 0.05 % m/m sulphur, and less than 10 % by mass aromatics. The fuel may have on average more than 0.9 alkyl branches per paraffinic molecule as measured by H+ NMR analysis. The invention also provides a method for operating a CI engine to produce low particulates emissions, which method comprises combusting the fuel with oxygen or an oxygen containing gas in the engine. Yet further the invention provides a method of improving the conversion efficiency of oxidation catalysts used in conjunction with CI engines, said method including combusting the fuel in the CI engine in the presence of said oxidation catalysts and in oxygen or an oxygen containing gas.

WO 03/104361 A2

SYNTHETIC FUEL WITH REDUCED PARTICULATE MATTER EMISSIONS AND A METHOD OF OPERATING A COMPRESSION IGNITION ENGINE USING SAID FUEL IN CONJUNCTION WITH OXIDATION CATALYSTS

5 **FIELD OF THE INVENTION**

This invention relates to a synthetic compression ignition engine fuel, to a method of making that fuel, and to a method of operating a compression ignition engine using said fuel, and in conjunction with oxidation catalysts.

10 **BACKGROUND OF THE INVENTION**

It has been stated that the potential impact of a fuel on diesel emissions has been recognized by state and federal regulatory agencies, and fuel specifications have now become a part of emissions control legislation. Studies both in the U.S. and in Europe have concluded that particulate
15 emissions are generally a function of fuel sulfur content, aromatics content and cetane number. Consequently, the U.S. Environmental Protection Agency has set a limit on diesel fuel sulfur content of 0.05 wt % as well as a minimum cetane number of 40, with even stricter limits on sulphur content being envisaged in the future. Additionally, the state of California has set a 10 vol %
20 maximum on aromatics content. Also, alternative fuels are beginning to play more of a role for low emissions vehicles. Thus, the search for efficient, clean burning fuels, particularly with low particulate emissions remains ongoing.

Epidemiological investigations have suggested an association between health effects and ambient suspended particulate matter. These studies have
25 associated disease incidence with particulate matter exposure. Research is continuing in many areas to identify a biological mechanism whereby this association can be explained, but as yet there are only hypotheses. Lung responses to particles in the 50 nm size range have been identified, where there are none when the same material is introduced as 250 nm particles.
30 This has lead to the suggestion that adverse health effects are associated

with the ultrafine particle fraction, and has promoted interest in the potential health effects of the particle itself, rather than any chemical property of the particle.   Thus the number of nanoparticles emitted is possibly of greater importance than the composition of the particle.

5   Typically, diesel particle emissions have a bimodal size distribution, when particle number emissions are plotted on a logarithmic scale. The first mode is associated with particles formed by accumulation, and has a peak in the size range between 500 and 50 nm. These particles are referred to as ultrafine particles. The second peak is in the size range between 50 and 5

10   nm, and is associated with particles formed by nucleation. Particles in this size range are generally referred to as nanoparticles. Further distinction is made between fine particles (or PM2.5, diameter < 2 500 nm), and PM10 (diameter < 10 000 nm).

The accumulation mode particles account for most of the mass of diesel

15   particulate emissions, while the greatest numbers of particles are found in the nanoparticle size range.

The concerns regarding the health effects of very small particles have been compounded by observations that modern diesel engines, while emitting lower particle mass concentrations than older engines, may actually emit

20   higher particle number concentrations than the older engines. Most of the particles emitted are in the nanoparticle size range, and it has been suggested that the reason for increased number of these particles is that the nucleation and growth of nanoparticles is suppressed by the presence of existing carbon particles which are found in the accumulation mode size

25   range. Thus, older engines with higher particulate mass emissions can display lower nanoparticle number emissions. Since it has been demonstrated that the use of synthetic diesel fuels results in lower particulate mass emissions than conventional crude oil-derived diesel fuels, it is possible that the same mechanism may result in higher particle number concentrations being emitted

30   with these fuels.

Surprisingly, after extensive research, the applicant has now developed a fuel having a composition which results in superior nanoparticle number emission properties compared to low sulphur crude oil-derived diesel fuel.

SUMMARY OF THE INVENTION

5   In this specification whenever the term diesel fuel is used it is intended to include any middle distillate cut useful in a compression ignition engine (CI engine).

In accordance with this invention there is provided a compression ignition (CI) engine fuel derived from a Fischer-Tropsch process, which fuel has a
10   generally increasing iso:n paraffins ratio with increasing paraffin carbon number at least between C_9 to C_{18}, less than 0.05% m/m sulphur, and less than 10% by mass aromatics.

Said CI engine, when combusting said fuel, emitting particulates having a maximum number weighted particle size distribution of less than 1×10^8
15   particles per cm^3 between 10nm and 20nm particle size.

The iso:n paraffins ratio may generally increase with increasing paraffin carbon number at least between C_9 to C_{24}.

The particulates which are emitted may have a particle size distribution in which fewer nanoparticles are produced than that emitted when a diesel fuel
20   derived from crude oil is combusted in a compression ignition engine.

The fuel may contain predominantly branched paraffins, that is, ≥50 mass% iso-paraffins, typically > 55 mass%, and more typically ≥60 mass% iso-paraffins.

The iso-paraffin to n-paraffin mass ratio may be from 1:1 to 4:1, typically from
25   3:2 to 3:1, generally 2:1.

In one embodiment the iso-paraffin to n-paraffin mass ratio is 21:10.

The fuel may be predominantly C_8 to C_{24} material.

The fuel may be predominantly $C_9 - C_{22}$.

The fuel may include in excess of 70 mass% of C_{12} and heavier.

The fuel may have an average carbon number of between 13 and 19, typically about 15.

5   The fuel may have on average more than 0.9 alkyl branches per paraffinic molecule as measured by H^+ NMR analysis.

The fuel may have more than 1 alkyl branch per paraffinic molecule.

The fuel may be substantially oxygenate free, typically having less than 0.1% oxygen. The fuel may have less than 0.01% and typically less than 0.005% oxygen.

10   The fuel may have a cetane number of at least 55, typically at least 65. The fuel may have a cetane number of 74.

The invention extends to a diesel fuel which, when combusted in a compression ignition engine under normal combustion conditions, results in emissions having a reduction of more than 70% in the number of particles in
15   the ≤50 nm size range, when compared to a low sulphur crude oil-derived diesel fuel combusted under similar conditions.

The reduction may be greater in the ≤30 nm range.

The fuel may have characteristics as set out in Table 1 below:

Table 1: Composition and Characteristics of the Synthetic Diesel Fuel

Property		Value
Specific Gravity, 60°F		0.765
Nitrogen	ppm	< 1
Sulfur	ppm	< 1
Cloud Point	°C	-18
Cetane Number		74.8

Total Aromatics (wt %)	wt %	< 1.0
GC-MS Analysis		
▪ Paraffins, wt%	wt %	100
▪ Paraffin iso/n ratio	Mass	2.1
▪ Olefins, wt%	wt %	0
▪ Percent of material C12-C24	Mass	80.7
▪ Average Carbon Number		15.2
▪ Alkyl branches/molecule		1.0
Distillation (D-86, vol %)		
IBP	°C	169
10	°C	187
50	°C	251
90	°C	312
FBP	°C	329

The branching characteristics of the fuel are summarized in table 2 below:

Table 2: Branching Characteristic of Low Emission Diesel Fuel

	Paraffins			iso/n-paraffin
	n-paraffins %	Iso-paraffins %	Total	Ratio
C9	2.96	0.00	2.96	---
C10	3.59	4.24	7.83	1.18
C11	3.80	4.65	8.45	1.22

C12	3.65	4.77	8.42	1.31
C13	3.41	5.34	8.75	1.57
C14	3.00	5.34	8.34	1.78
C15	2.61	5.56	8.17	2.13
C16	2.33	8.65	10.98	3.71
C17	1.99	5.74	7.72	2.89
C18	1.51	6.11	7.62	4.04
C19	1.60	5.98	7.58	3.73
C20	1.18	5.35	6.53	4.52
C21	0.58	3.82	4.41	6.54
C22	0.22	2.00	2.23	8.94

According to a further aspect of the invention, there is provided a method of improving the conversion efficiency of oxidation catalysts used in conjunction with compression ignition engines, said method including combusting a

5   compression ignition engine fuel as described above in the compression ignition engine in the presence of said oxidation catalysts and oxygen or an oxygen containing gas.

The method may include the operation of the compression ignition engine at idling and low engine loads.

10   The compression ignition engine fuel may be a synthetic Fischer-Tropsch derived fuel which may in turn be a GTL diesel fuel.

According to a further aspect of the invention there is provided a method for operating a compression ignition (CI) engine to produce low particulate emissions, which method comprises combusting a CI engine fuel substantially

15   as described above with oxygen or an oxygen containing gas in a CI engine.

Said CI engine, when combusting said fuel emitting particulates having a maximum number weighted particle size distribution of less than 1×10^8 particulates per cm^3 between 10nm and 20nm particle size,.

5   The particulates which are emitted may have a particle size distribution in which fewer nanoparticles are produced than that emitted when a diesel fuel derived from crude oil is combusted in a compression ignition engine.

DESCRIPTION OF EMBODIMENTS OF THE INVENTION

The invention will now be illustrated, by way of non-limiting examples only, with reference to the accompanying Figure 1.

10   **Figure 1 – FT work-up process**

A FT work-up process is outlined in the attached Figure 1. The synthesis gas (syngas), a mixture of Hydrogen and Carbon Monoxide, enters the FT reactor 1 where the synthesis gas is converted to hydrocarbons by the FT process.

A lighter FT fraction is recovered in line 7, and may or may not pass through
15   fractionator 2 and hydrotreater 3. The product 9 (9a) from the hydrotreater may be separated in fractionator 4 or, alternatively, mixed with hydrocracker 5 products 16 and sent to a common fractionator 6.

A waxy FT fraction is recovered in line 13 and sent to hydrocracker 5. If fractionation 2 is considered then the bottoms cut 12 is also sent to
20   hydrocracker 5. The products 16, on their own or mixed with the lighter fraction 9a, are separated in fractionator 6.

Depending on the process scheme, a light product fraction, naphtha 19, is obtained from fractionator 6 or by blending equivalent fractions 10 and 17. This is a C_5-160°C fraction useful as naphtha.

25   A somewhat heavier cut i.e. the middle cut, synthetic diesel 20, is obtainable in a similar way from fractionator 6 or by blending equivalent fractions 11 and 18. This cut is recovered as a 150-370°C fraction useful as diesel

The heavy unconverted material 21 from fractionator 6 is recycled to extinction to hydrocracker 5. Alternatively, the residue may be used for

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production of synthetic lube oil bases. A small amount of C_1-C_4 gases is also separated in fractionator 6.

The described FT work-up process of Figure 1 may be combined in a number of configurations. The applicant considers these an exercise in what is known 5　in the art as Process Synthesis Optimisation.

FIGURE 1
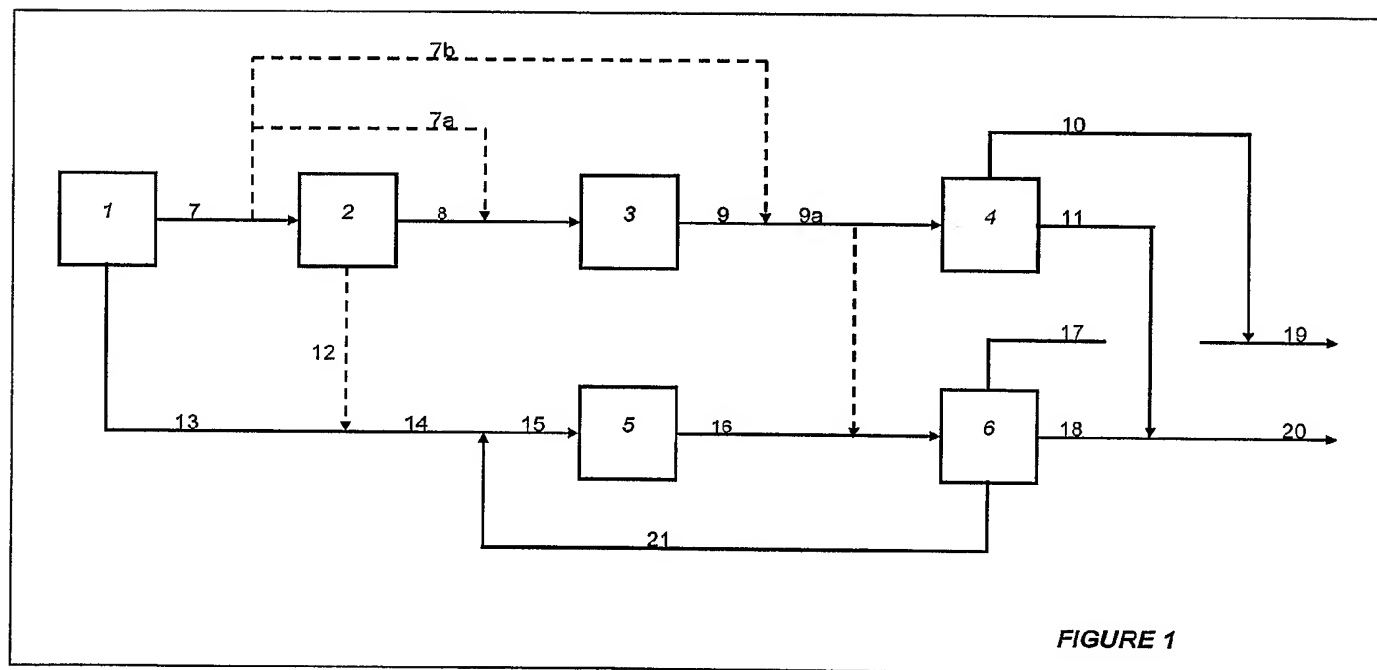
Examples of Use of Low Emission Diesel Fuel

Tests were conducted using the fuels of the invention:

EXAMPLE 1: Particle Number Emissions

For the purposes of comparing particle number emissions and size distributions, a commercially available, low sulphur diesel fuel approved by the US Environmental Protection Agency for on-highway use, was used as the reference fuel. Important characteristics of the two test fuels are presented in Table 3.

Table 3: Analysis of Test Fuels

Property	Test Method	Low-S Diesel Reference Fuel	Synthetic Diesel Fuel
Specific Gravity, 60°F	ASTM D4052	0.8705	0.7647
Kinematic Viscosity., 40°C (cSt)	ASTM D445	3.199	2.007
Flash Point (°C)	ASTM D93	82	60
Cloud Point (°C)	ASTM D2500	-19	-18
Total Sulphur (ppm)	ASTM D2622	404	<1
Distillation (°C)	ASTM D86		
IBP		196	169
10%		223	187
50%		273	251
90%		330	312
FBP		359	329
Cetane Number	ASTM D613	41.5	74.8

Total Aromatics (wt %)	ASTM D5186	38.4	<1.0
Oxygen as Oxygenates according to GC-MS analysis, (ppm)			<6
Oxygen as primary C12 - C24 alcohol (ppm)			<6
Oxygen as primary C7 - C12 alcohol (ppm)			<6

Exhaust particle number emissions and size distributions were measured using two test engines, a heavy-duty diesel engine, and a passenger car diesel engine.

5   The heavy-duty diesel engine was a Caterpillar™ model C12 modified to be compliant with 1998 US emission levels. This engine is a 6 cylinder, 12 liter, turbocharged, after-cooled diesel engine rated at 312 kW at 2100 rev/min, with a peak torque of 2237 Nm at 1200 rev/min. A 5W-40 synthetic lubricating oil, which had been aged for 40 hours, was used in the engine during the 10   tests.

The passenger car engine was a 1999 Volkswagen™ TDI diesel engine. This engine is a 4 cylinder, 1.9 liter, turbocharged, charge-air cooled diesel engine, rated at 66 kW. The standard exhaust aftertreatment equipment, in the form of an oxidation catalyst, was fitted for the tests. A 5W-40 synthetic 15   lubricating oil, which had approximately 125 hours of running time in the engine at the onset of testing, was used in the engine during the tests.

The test. engines were fully warmed up and operated under steady-state conditions while the measurements were conducted. The heavy-duty engine was tested at four different speed and load settings, while the passenger car 20   engine was tested at five different speed and load settings. The speed and load settings used for the two engines are presented in Table 4. For each

fuel, one set of measurements was made per day for three consecutive days, and the results averaged to obtain the final size distribution for each test mode. For the purposes of illustration, a single composite size distribution was then obtained for each engine and fuel, by averaging the size

5   distributions from each test mode.

Table 4: Engine Test Modes

Mode Number	Heavy-duty Engine		Passenger Car Engine	
	Speed (rev/min)	Load (Nm)	Speed (rev/min)	Load (Nm)
1	1 700	569	2 620	72
2	1 400	366	2 500	152
3	1 200	814	1 900	101
4	800	idle	1 400	40
5	-	-	1 200	idle

Particle size distributions in the exhaust were measured by means of a micro-dilution device, a Scanning Mobility Particle Sizer (SMPS), and a

10   Condensation Particle Counter (CPC). The SMPS measures particle electric mobility diameter and the CPC measures particle number concentrations in the diameter range of 7 to 300 nm in a 4-minute (2 minutes up, 2 minutes down) scan time. This particle measurement system consists of a neutralizer, a mobility section, a TSI model 3010 CPC, and a computerized control and

15   data acquisition system. The dilution system is described in more detail in SAE Paper 1999-01-1142, 1999 by Abdhul-Khalek, I.S., Kittelson, D.B., and Brear, F., "The Influence of Dilution Conditions on Diesel Exhaust Particle Size Distribution Measurements", and SAE Paper 1999-01-1142, 1999 by Abdhul-Khalek, I.S., Kittelson, D.B., and Brear, F., "The Influence of Dilution

20   Conditions on Diesel Exhaust Particle Size Distribution Measurements".

The micro-dilution tunnel pre-conditions the exhaust sample before the sample enters the SMPS. In the configuration used in these tests, the first-stage dilution temperature was held constant at approximately 40°C for the heavy duty engine tests, and 30°C for the passenger car engine tests.

The two-stage air ejector exhaust dilution system is designed to allow variation of the residence time in the primary dilution stage, before secondary dilution. For these tests, a relatively short residence time (0.8 seconds) in the micro-dilution tunnel was maintained. The exhaust enters a sampling probe
5   that is immersed in the exhaust flow and then passes through a short section of stainless steel tube that is insulated and heated to keep the sample temperature and the exhaust temperature equal. Downstream of the sample line, an ejector pump with a flow orifice provides the first stage (primary) dilution. The ejector pump consists of a compressed air inlet, sample inlet
10   (orifice location), and one outlet. Filtered and compressed air at 276 kPa (40 psi) is used to drive the ejector pump, which in turn draws an exhaust sample flow through the orifice. This air then mixes with the exhaust sample providing primary dilution. The primary dilution ratio varied between 9:1 and 12:1.

The secondary dilution stage is designed to halt additional particle growth and
15   to provide a final particle number concentration in the dilute exhaust sample within the measurement range of the CPC. Filtered, compressed air at 207 kPa (30 psi) is used to drive the ejector pump, which draws an exhaust sample flow through an orifice, from the micro-dilution tunnel. The secondary dilution ratio varied between 19:1 and 22:1.

20   The composite, number weighted, particle size distributions for the synthetic diesel fuel and the reference fuel, are shown in Figures 2 and 3, for the heavy-duty engine and the passenger car engine, respectively. As the ranges of the measured particle number emissions and sizes are large, the graphs are plotted with logarithmic axes.

25   It can be seen that with both engines, the particle size distributions with the reference fuel have distinctive bimodal size distributions, with both the nucleation mode and the accumulation mode being present. It can also be seen that, with both engines, the numbers of particles in the size range below approximately 30 nm are significantly lower with the synthetic diesel fuel, than
30   with the low sulphur reference diesel fuel. Because most of the particle number emissions are concentrated in this size range, this has the consequence that the total particle number emissions are also significantly

lower with the synthetic diesel fuel, than with the low sulphur diesel fuel. These findings are summarized in Figure 4, which shows a comparison of the integrated particle numbers in the size ranges below 30 nm, below 50 nm, and below 300 nm. It can be seen that for both engines, there are reductions in the number of particles emitted in these different size classifications, of greater than 65%.
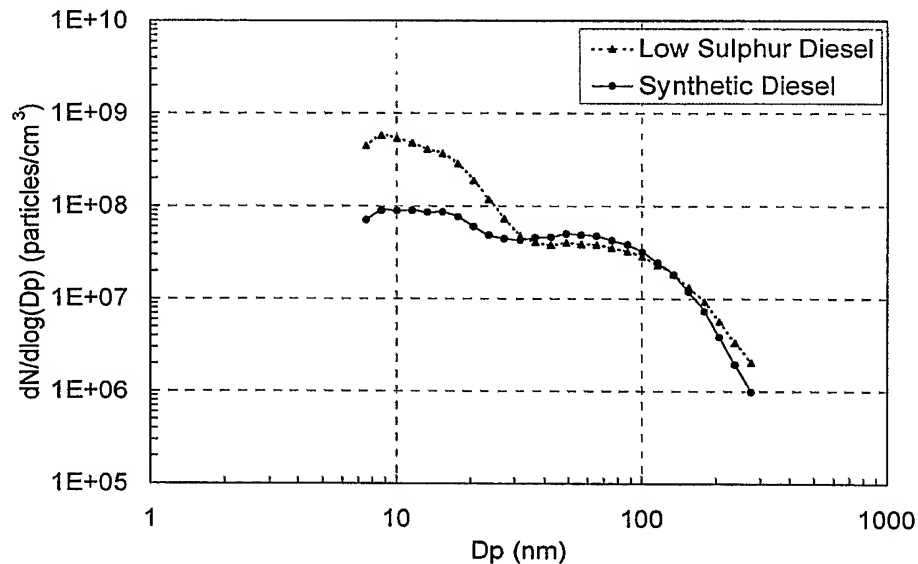
Figure 2:   Number Weighted Particle Size Distribution with Synthetic Diesel Fuel and Low Sulphur Diesel Fuel, for the Caterpillar C12 Heavy-duty Diesel Engine
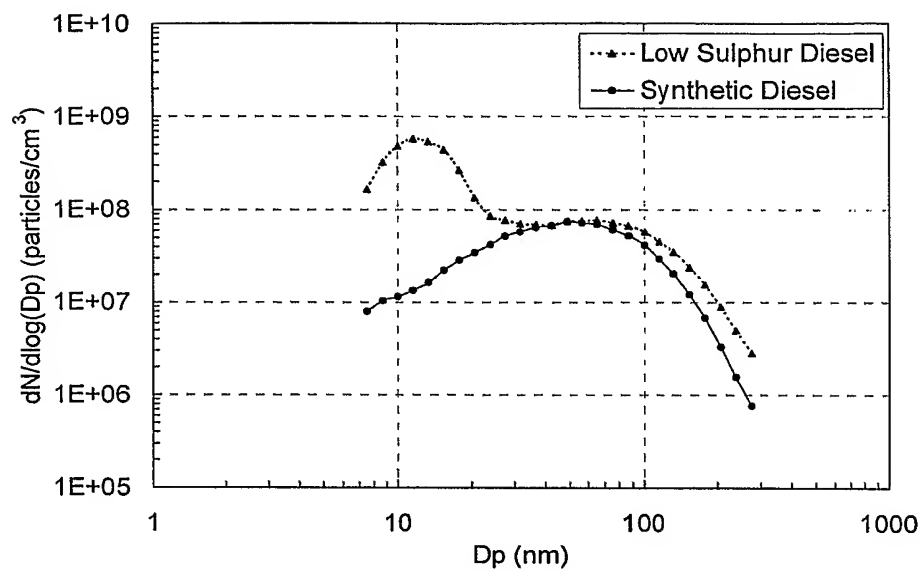
Figure 3:   Number Weighted Particle Size Distribution with Synthetic
             Diesel Fuel and Low Sulphur Diesel Fuel, for the VW Tdi
             Passenger Car Diesel Engine
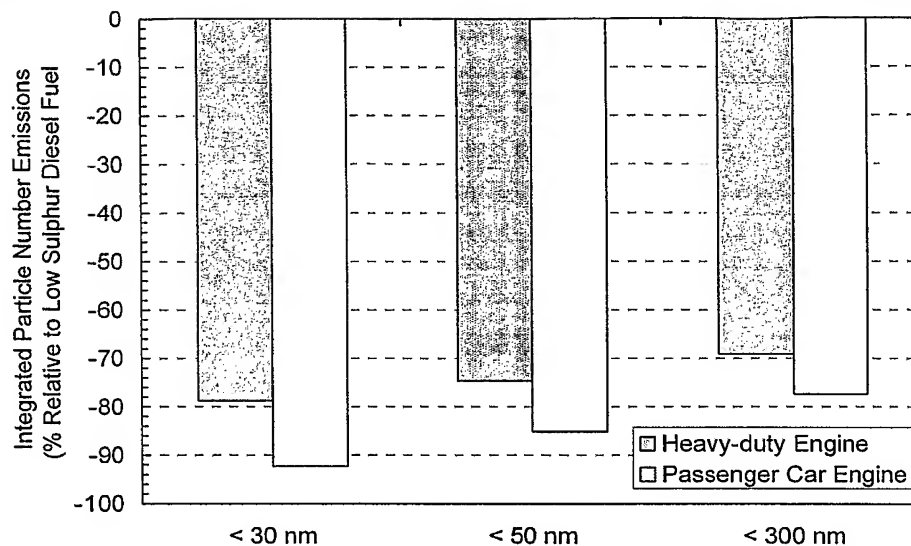
Figure 4:   Relative Integrated Particle Number Emissions for Various
             Size Ranges of Particles

Regulated Exhaust Emissions

For the purposes of comparing regulated exhaust emissions, a fuel meeting
the US Environmental Protection Agency requirements for low sulphur diesel
5   fuel for on-highway use, was used as the reference fuel in the tests.
Important characteristics of the reference fuel and the synthetic diesel fuel are
shown in Table 5.

Table 5: Properties of Test Fuels

Property	Test Method	Low Sulphur Diesel Reference Fuel	Synthetic Diesel Fuel
Density at 15°C (kg/l)	ASTM D4052	0.8457	0.7769
Distillation (°C)	ASTM D86		
▪ IBP		184	189
▪ 10%		214	209

		259	256
▪ 50%			
▪ 90%		312	331
▪ FBP		342	356
Viscosity at 40°C (cSt)	ASTM D445	2.35	2.43
Cetane Number	ASTM D613	40.3	> 73.7
Total Sulphur (mass %)	ASTM D4294	0.022	0.001
Total Aromatics (mass %)	HPLC	42.78	0.47
Polynuclear Aromatics (mass %)		9.39	0.03
Cloud Point (°C)	ASTM D2500	-18	-29
CFPP (°C)	IP 309	-21	-37

Regulated exhaust emissions were measured using the diesel engine described in Table 6. This unit was modified and calibrated to meet the 1991 US emission standards. Hot-start transient emission tests were conducted in accordance with the EPA Federal Test Procedure (FTP) as specified in the Code of Federal Regulations (CFR), Title 40, Part 86, Subpart N. Testing procedures incorporated instrumentation and sample system calibrations, engine performance checks, gaseous and particulate emissions sampling and measurement, and transient test performance evaluations. The emissions measured included unburned hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides (NOx), and particulate matter (PM).

Three hot-start tests were performed with each fuel, and the results presented represent the averaged values from the three tests. The transient torque map that was used during the tests was generated using the synthetic fuel, thereby ensuring that peak engine loads attained during test runs would be similar for both fuels.

Table 6: Characteristics of 1988 DDC Series 60 Engine

Engine configuration	In-line 6 cylinder,
Displacement	12.7 liter (130 mm bore, 160 mm stroke)
Aspiration	Turbocharged, intercooled
Rated Power	261 kW at 1800 rev/min
Rated Torque	1830 Nm at 1200 rev/min
Fuel Injection	Direct injection, electronically controlled unit injectors
Restrictions for Transient Cycle	Inlet : 4.0 kPa Exhaust : 9.5 kPa
Low idle speed	600 rev/min

The results of the emission tests are presented numerically in Table 7, and are compared between the two test fuels graphically in Figure 5.

5   **Table 7:   Results of Transient Hot-Start Emission Tests**

Emission	Hot Start Transient Emissions (g/kWh)	
	Low Sulphur Diesel Fuel	Synthetic Diesel Fuel
HC Mean value	0.215	0.094
▪ Std. Deviation	0.011	0.006
▪ Coeff. of Var., %	5.1	6.4
CO Mean value	3.829	2.571
▪ Std. Deviation	0.100	0.042
▪ Coeff. of Var., %	2.6	1.6

NOx Mean value	7.050	5.081
▪ Std. Deviation	0.033	0.049
▪ Coeff. of Var., %	0.5	1.0
PM Mean value	0.277	0.217
▪ Std. Deviation	0.006	0.003
▪ Coeff. of Var., %	2.2	1.4

It can be seen that with the synthetic diesel fuel produced significantly lower emissions relative to the low sulphur diesel fuel.
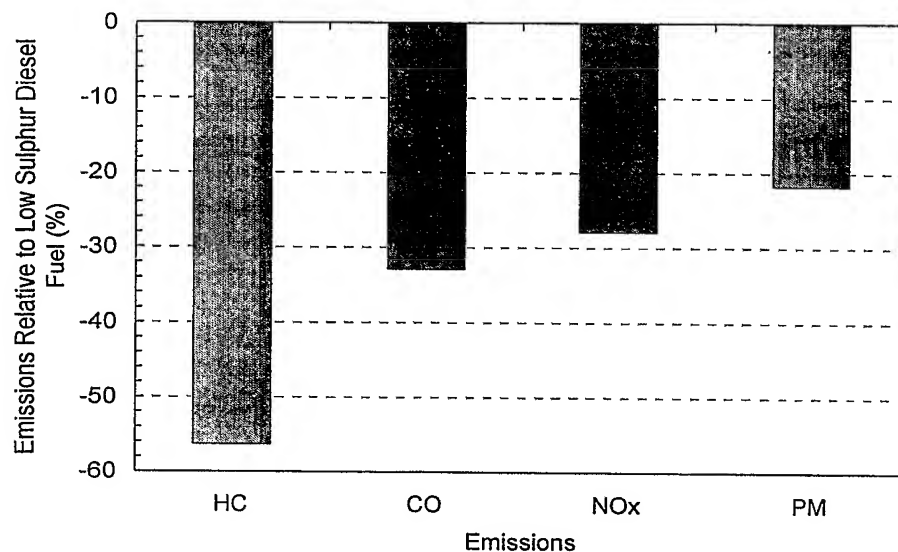

Figure 5:   Regulated Exhaust Emissions with Synthetic Diesel Fuel, relative to Low Sulphur Diesel Fuel

5   **EXAMPLE 2: OXIDATION CATALYST PERFORMANCE TESTS**

Various exhaust emission tests were carried out to compare a Japanese low sulphur diesel fuel derived from crude oil and GTL diesel fuel, a synthetic compression ignition fuel of the present invention. The tests focused on

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regulated emissions of hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides (NOx) and particulate matter (PM), as well as carbon dioxide (CO_2). The emission tests were performed on a Japanese heavy-duty vehicle, and tests were conducted both with and without an oxidation catalyst fitted in the
5   vehicle exhaust.

The types of emission tests performed were a Japanese 13 mode steady-state test cycle for heavy-duty engines, and modes 2, 5, and 8 of the Tokyo test cycle, a special test cycle representative of congested traffic patterns encountered in the Tokyo inner city environment.

10   The properties of the synthetic diesel fuel used for the tests were typical of diesel produced by low temperature Fischer-Tropsch processes, with a very high cetane number (> 70), very low sulphur (< 1 ppm), and a very low aromatics content (< 1 %). In addition, the GTL diesel used in this study also has good natural cold flow properties (CFPP < -20 °C). The reference diesel
15   fuel used had a sulphur content of 29 ppm, an aromatics content of 21 %, and a cetane number of 57.5. The properties of the test fuels are shown in Table 8.

Table 8: Physical Properties of the Test Fuels

Property		Test Method	GTL Diesel	Japanese Low Sulphur Diesel (50 ppm sulphur specification)
Feedstock		-	Natural gas	Crude oil
Sulphur	ppm (mass)	JIS K 2541	<1	29

Density at 15˚C	**kg/ℓ**	JIS K 2249	0.7680	0.8185
Viscosity at 30˚C	**mm²/s**	JIS K 2283	2.335	2.770
Cloud Point	**˚C**	JIS K 2269	-20	-11
Cold Filter Plugging Point	**˚C**	JIS K 2288	-30	-22.5
Lower Heat of Combustion	**MJ/kg**	JIS K 2279	43.72	43.26
	MJ/ℓ @ 15˚C	calculated	33.58	35.41
Cetane Number		JIS K 2280	74.1	57.5
Cetane Index		JIS K 2280	79.8	57.4
Distillation	**IBP**	**˚C**		159.5	179.5
	10 %	**˚C**		183.5	204.0
	30 %	**˚C**		214.0	233.0
	50 %	**˚C**	JIS K 2254	248.5	259.0
	70 %	**˚C**		282.0	283.5
	90 %	**˚C**		314.0	317.5
	95 %	**˚C**		324.0	330.0
	FBP	**˚C**		334.0	344.5

HPLC	Saturates	% (mass)	JPI 5S-49-97	99.9	78.7
	Olefins	% (mass)		0.0	0.1
	Total aromatics	% (mass)		0.1	21.2
	1-aromatics	% (mass)		0.1	18.7
	2-aromatics	% (mass)		0.0	2.3
	+3-aromatics	% (mass)		0.0	0.1
CHN Content	C	% (mass)	ASTM D 5291	85.0	86.1
	H	% (mass)		14.9	13.8
	N	ppm (mass)		<3	5

Details of the test vehicle are given in Table 9, and details of the emission test cycles are given in Table 10 for the 13 mode test, and Figure 6 for modes 2, 5, and 8 of the Tokyo test cycle.

5   Table 9: Heavy-Duty Test Vehicle

Vehicle Type		Truck
Model Year		1998
Vehicle Weight	kg	2 808
Equivalent Inertia Weight	kg	6 025
Engine		In-line 5 cylinder

Displacement	ℓ	6.634
Compression Ratio		19.2 : 1
Fuel Injection		DI, In-line injection pump
Aspiration		Natural
Peak Power	kW @ r/min	125 @ 2900
Peak Torque	Nm @ r/min	450@ 1 600
Equipment for low emissions		EGR
		Oxidation catalyst

Table 10: Japanese 13-Mode Steady-State Emission Test Cycle for Heavy-Duty Engines

Mode	Speed (% of rated)	Load (% of rated)	Weighting Factor
1	idle	-	0.205
2	40	20	0.037
3	40	40	0.027
4	idle	-	0.205
5	60	20	0.029

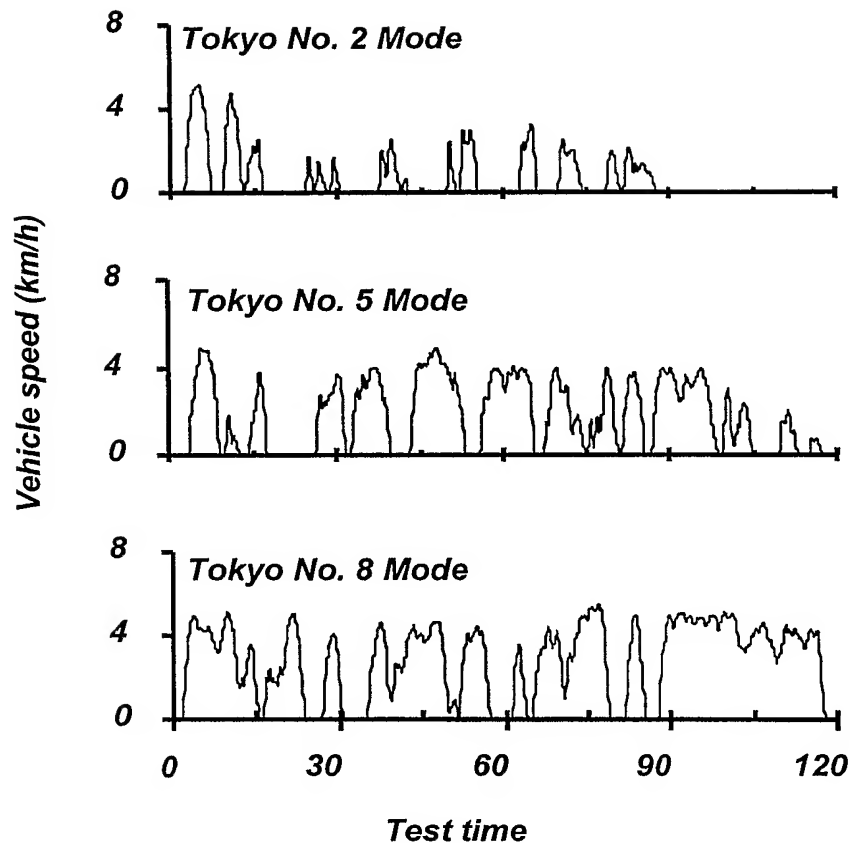| 6	60	40	0.064
7	80	40	0.041
8	80	60	0.032
9	60	60	0.077
10	60	80	0.055
11	60	95	0.049
12	80	80	0.037
13	60	5	0.142

Figure 6: Modes 2, 5, and 8 of Tokyo Emission Test Cycle

During testing, the exhaust gas was diluted with purified air, supplied at a temperature of 25 °C and a relative humidity of 50%, in a dilution tunnel. The exhaust gas measurement system (Horiba VETS-9000) included an exhaust gas analyser (Horiba MEXA-9400F), a constant volume sampler (CVS-120T)

5   and a low-volume sampler (LVS). A glass fibre filter (Pallflex TX40HI20-WW) of 70 mm diameter was used for sampling PM in the LVS.

The results of each of the emission tests are presented in Tables 11, 12, 13, and 14. It can be seen that, in general, all of the regulated emissions (HC, CO, NOx, and PM) are lower with the GTL diesel fuel, when compared to the

10   Japanese low sulphur diesel fuel. Also shown in each table, is the apparent conversion efficiency of the oxidation catalyst fitted in the vehicle exhaust. This is defined as the difference in emission level measured with and without the catalyst fitted, expressed as a percentage of the emission level without the

catalyst fitted. The oxidation catalyst is fitted to primarily to reduce HC, CO, and PM emissions, and the conversion efficiencies for NOx are therefore not indicated.

It can be seen that the conversion efficiencies measured with the GTL diesel fuel for HC and CO are always higher than those measured with the low sulphur diesel. The conversion efficiency for PM was lower with the GTL fuel for Mode 8 of the Tokyo test cycle, but higher for all other tests. The averaged conversion efficiencies for all of the tests are shown in Table 15, where it can be seen that the conversion efficiency with the GTL diesel fuel was higher than that of the Japanese low sulphur diesel by 29, 27, and 3 percentage points, for HC, CO, and PM, respectively.

Table 11: Results for 13-Mode Heavy-Duty Test Cycle

Oxidation Catalyst			Without		With		Conversion Efficiency	
Fuel			LSD	GTL diesel	LSD	GTL diesel	LSD	GTL diesel
Emissions	THC	g/kWh	0.84	0.91	0.26	0.20	69%	78%
	CO	g/kWh	2.55	2.00	0.78	0.31	69%	85%
	NOx	g/kWh	4.93	4.21	4.64	4.07	-	-
	PM	g/kWh	0.17	0.14	0.14	0.11	18%	21%

Table 12: Results for Mode 2 of the Tokyo Test Cycle

Oxidation Catalyst			Without		With		Conversion Efficiency	
Fuel			LSD	GTL diesel	LSD	GTL diesel	LSD	GTL diesel
Emissions	THC	g/kWh	0.59	0.37	0.24	0.08	59%	78%
	CO	g/kWh	1.73	1.09	1.35	0.41	22%	62%
	NOx	g/kWh	3.76	3.23	3.56	3.08	-	-
	PM	g/kWh	0.09	0.06	0.06	0.04	33%	33%

Table 13: Results for Mode 5 of the Tokyo Test Cycle

Oxidation Catalyst			Without		With		Conversion Efficiency	
Fuel			LSD	GTL diesel	LSD	GTL diesel	LSD	GTL diesel
Emissions	THC	g/kWh	1.21	0.82	0.73	0.07	40%	91%
	CO	g/kWh	0.40	0.29	0.18	0.05	55%	83%
	NOx	g/kWh	2.61	2.22	2.45	2.12	-	-
	PM	g/kWh	0.07	0.05	0.05	0.03	29%	40%

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Table 14: Results for Mode 8 of the Tokyo Test Cycle

Oxidation Catalyst			Without		With		Conversion Efficiency	
Fuel			LSD	GTL diesel	LSD	GTL diesel	LSD	GTL diesel
Emissions	THC	g/kWh	1.21	0.82	0.73	0.07	31%	67%
	CO	g/kWh	0.4	0.29	0.18	0.05	64%	91%
	NOx	g/kWh	2.61	2.22	2.45	2.12	-	-
	PM	g/kWh	0.07	0.05	0.05	0.03	25%	20%

Table 15: Averaged Oxidation Catalyst Conversion Efficiencies for CO, HC, and PM

Fuel			LSD	GTL diesel
Emissions	THC	g/kWh	50%	79%
	CO	g/kWh	53%	80%
	PM	g/kWh	26%	29%

The following acronyms and abbreviations are used in the above example:

CHN: Carbon, hydrogen and nitrogen

CO: Carbon monoxide

CO2: Carbon dioxide

CVS: Constant volume sampler

DI: Direct injection

DPF: Diesel particulate filter

5 **EGR:** Exhaust gas recirculation

FBP: Final boiling point

GTL: Gas-to-liquids

HC: Unburned hydrocarbons

H/C Hydrogen/carbon ratio

10 **HPLC:** High pressure liquid chromatography

IBP: Initial boiling point

IC: Intercooled

LVS: Low volume sampler

NOC: Nippon Oil Corporation

15 **NOX:** Oxides of nitrogen

PM: Particulate matter

ppm: Parts per million

SOF: Soluble organic fraction

SPD: Slurry Phase Distillate

20 **TC:** Turbocharging

THC: Total Unburned Hydrocarbons

Without admitting them as prior art, the following articles are incorporated herein by reference, as if specifically reproduced here in their totality, in order to improve in understanding the invention and the examples:

1.   Abdul-Khalek, I., et al, "Diesel Exhaust Particle Size : Measurement Issues and Trends".   SAE Paper 980525, Society of Automotive Engineers, 1998.

2.   Schaberg, P.W., et al, "Diesel Exhaust Emissions Using Sasol Slurry Phase Distillate Process Fuels".   SAE Paper 972898, Society of Automotive Engineers, 1997.

3.   Khalek, I., Kittelson, D.B., and Brear, F., "Nanoparticle Growth during Dilution and Cooling of Diesel Exhaust: Experimental Investigation and Theoretical Assessment". SAE Paper 2000-01-0515, 2000.

4.   Abdhul-Khalek, I.S., Kittelson, D.B., and Brear, F., "The Influence of Dilution Conditions on Diesel Exhaust Particle Size Distribution Measurements". SAE Paper 1999-01-1142, 1999.

5.   Abdhul-Khalek, I.S., Kittelson, D.B., and Brear, F., "The Influence of Dilution Conditions on Diesel Exhaust Particle Size Distribution Measurements". SAE Paper 1999-01-1142, 1999.

6.   Schaberg, P.W., Myburgh, I.S., Botha, J.J., Roets, P.N.J., Voljoen, C.L., Dancuart, L.P., and Starr, M.E., "Diesel Exhaust Emissions Using Sasol Slurry Phase Distillate Process Fuels".   SAE Paper 972898, 1997.

Claims

1.   A compression ignition (CI) engine fuel derived from a Fischer-Tropsch process, which fuel has a generally increasing iso:n paraffins ratio with increasing paraffin carbon number at least between C_9 to C_{18}, less than

5   0.05% m/m sulphur, and less than 10% by mass aromatics.

2.   A compression ignition engine fuel as claimed in claim 1, which fuel has on average more than 0.9 alkyl branches per paraffinic molecule as measured by H^+ NMR analysis.

3.   A compression ignition engine fuel as claimed in claim 2, wherein the

10   fuel has more than 1 alkyl branch per paraffinic molecule.

4.   A compression ignition engine fuel as claimed in any one of claims 1 to 3, wherein the iso:n paraffins ratio generally increases with increasing paraffins carbon number at least between C_9 to C_{24}.

5.   A compression ignition engine fuel as claimed in any one of the

15   preceding claims, which fuel comprises ≥50 mass% iso-paraffins.

6.   A compression ignition engine fuel as claimed in any one of the preceding claims, which fuel comprises > 55 mass% iso-paraffins.

7.   A compression ignition engine fuel as claimed in any one of the preceding claims, which fuel comprises ≥60 mass% iso-paraffins.

20   8.   A compression ignition engine fuel as claimed in any one of the preceding claims, wherein the iso-paraffin to n-paraffin mass ratio is from 1:1 to 4:1.

9.   A compression ignition engine fuel as claimed in any one of the preceding claims, wherein the iso-paraffin to n-paraffin mass ratio is from 3:2

25   to 3:1

10.   A compression ignition engine fuel as claimed in any one of the preceding claims, wherein the iso-paraffin to n-paraffin mass ratio is 21:10.

11.   A compression ignition engine fuel as claimed in any one of the preceding claims, wherein the fuel is predominantly C_8 to C_{24} material.

12.   A compression ignition engine fuel as claimed in any one of the preceding claims, wherein the fuel is predominantly $C_9 - C_{22}$ material.

13.   A compression ignition engine fuel as claimed in any one of the preceding claims, wherein the fuel comprises in excess of 70 mass% of C_{12} and heavier.

14.   A compression ignition engine fuel as claimed in claim 13, wherein the fuel has an average carbon number of between 13 and 19.

15.   A compression ignition engine fuel as claimed in claim 14, wherein the fuel has an average carbon number of about 15.

16.   A compression ignition engine fuel as claimed in any one of the preceding claims, wherein the fuel is substantially oxygenate free having less than 0.1% oxygen.

17.   A compression ignition engine fuel as claimed in any one of the preceding claims, wherein the fuel is substantially oxygenate free having less than 0.005% oxygen.

18.   A compression ignition engine fuel as claimed in any one of the preceding claims, wherein the fuel has a cetane number of at least 55.

19.   A compression ignition engine fuel as claimed in claim 18, wherein the fuel has a cetane number of at least 65.

20.   A method of improving the conversion efficiency of oxidation catalysts used in conjunction with compression ignition engines, said method including combusting a compression ignition engine fuel as claimed in any one of claims 1 to 19 in a compression ignition engine in the presence of said oxidation catalysts and in oxygen or an oxygen containing gas.

21.   A method as claimed in claim 20, which includes the operation of the compression ignition engine at idling and low engine loads.

22.　　A method as claimed in claim 20 or 21, wherein the compression ignition engine fuel is a GTL diesel fuel.

23.　　A method for operating a compression ignition (CI) engine to produce low particulates emissions, which method comprises combusting a compression ignition engine fuel as claimed in any one of claims 1 to 19 with oxygen or an oxygen containing gas in a CI engine.

24.　　A method as claimed in claim 23, wherein said CI engine, when combusting said fuel, emits particulates having a maximum number weighted particle size distribution of less than 1×10^8 particles per cm^3 between 10nm and 20nm particle size,.

25.　　A method as claimed in claim 23 or claim 24, wherein the particulates which are emitted have a particle size distribution in which fewer nanoparticles are produced than that emitted when a diesel fuel derived from crude oil is combusted in a compression ignition engine.

26.　　A method as claimed in any one of claims 23 to 25, wherein the emissions may have a reduction of more than 70% in the number of particulates in the ≤50 nm size range when compared to a low sulphur crude oil-derived diesel fuel combusted under similar conditions.

27.　　A method as claimed in claim 26, wherein reduction may be greater in the ≤30 nm range.

28.　　A compression ignition engine fuel as claimed in claim 1, substantially as herein described and illustrated.

29.　　A method as claimed in claim 20 or 23, substantially as herein described and illustrated.

30.　　A new compression ignition engine fuel or a new method substantially as herein described.